The Improvement of Bitumen Properties by Adding NanoSilica

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Abstract

Asphalt oxidative aging is one of the prevalent causes of pavement distresses which increase pavement susceptibility to fatigue and low temperature cracking. This phenomenon is mainly studied through oxidation kinetics and through evaluating oxygen diffusivity rate into asphalt binders. While oxidative aging in pavement is inevitable, application of anti-aging additives shown to be an effective method in delaying oxidative aging. As such this paper investigates the merit of application of nano-silica as an anti-aging additive. To do so, different percentages of nano-silica was added to neat asphalt binder. Asphalt binder was then exposed to short term oxidative aging using a rolling thin film oven (RTFO). To study the change in the chemical, rheological and morphological properties of asphalt binders in presence of nano-silica, the Superpave™ tests, Fourier transform infrared spectroscopy (FTIR) as well as SEM imaging were conducted. The FTIR study shows that nano-silica can improve the aging resistance of the asphalt binder as reflected in lower level of carboxylic acids (observed at 1400-1440 cm-1) and sulfoxide (observed at ~1050 cm-1) in nano-silica modified specimen compared to those in non modified specimens. Carboxylic acids occur naturally in asphalt; however its concentration has been known to be increased significantly due to oxidative aging. This in turn reduces oxidation aging in modified asphalt. In addition, it was found that presence of nano-silica significantly increases the complex modulus (G*) and complex viscosity (η*) of the asphalt binder. This in turn improves pavement resistance to rutting. It was concluded that introduction of nano-silica to asphalt binder can improve the anti-aging property, rutting performance and rheological properties of asphalt binder.

Keywords

Nano-silica; Nano Modified Asphalt; Rheology; Aging

Introduction

The chemical composition of asphalt is quite complex, therefore, researchers mainly use percentages of SARA (**S**aturates, **A**sphaltene, **R**esin and **A**romatic) to compare various asphalt binder produced from different origins. Composition of each asphalt binder is typically grouped into two categories: asphaltenes and maltenes. The latter can be further subdivided into saturates, aromatics and resins (Petersen, 1984). However, asphalts colloidal system may change when it is exposed to oxygen at elevated temperature causing oxidative during asphalt production and service life. Aging has been known to be one of the principal factors expediting asphalt pavement's deterioration (Lu and Isacsson, 1998). The occurrence of asphalt binder aging is further expedited by thermal-oxidation during storage, mixing, transport and placing and compaction; this in turn negatively affects asphalt binder rheological properties causing pavement to be more susceptible to low temperature cracking (Lu and Isacsson, 2002; Gawel and Baginska, 2004). While pavement oxidative aging is inevitable, there have been many studies to better understand the oxidation mechanisms as well as to develop new methods and additives to delay oxidative aging. Among those additives are various resins, rubbers, polymers, sulphur, metal complexes, fibres, chemical agents and nano materials. The use of nano-materials has seen a tremendous development in recent years mainly due to their surface properties and their effectiveness in altering hierarchical structure of composite materials (You et al., 2011; Yao et al., 2012b; Onochie et al., 2013; Fini, 2013). It has been shown that introduction of certain nano-materials into asphalt binder could offer a significant improvement in asphalt physical and rheological properties leading to development of nano modified asphalt with superior performance. As such nanotechnology has been gradually incorporated into the field of modified asphalt with various kinds of nano-materials being used to modify asphalt in recent years. Nano-silica has been widely used in polymers and asphalt binder as inorganic filler to improve the properties of polymeric and bituminous materials (Zhou et al., 1999; Hu et al., 2004; Cheng et al., 2006; Liu and Pan, 2007). Over the

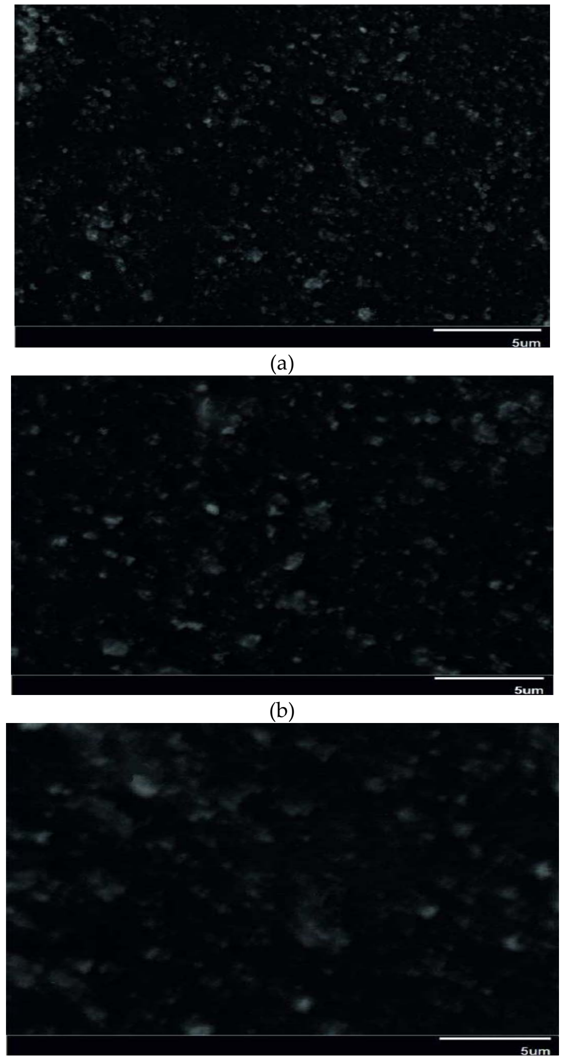
last 10 years, nano-silica has served as a promising material for designing and preparing new functional materials because of its high surface area and stability (Senff et al., 2009; Zhang and Islam, 2012; Kong et al., 2012; Singh et al., 2013). The shape and dimension of the silica particles are very desirable for application in asphalt binder mainly because the surface area of interaction is much higher than that of conventional fillers. By dispersing nano-silica into asphalt matrix one can create polymeric nano-composites with enhanced mechanical behavior, thermal and gas barrier properties (LeBaron et al., 1999; Sinha Ray and Okamoto, 2003; Yao et al., 2012a). Therefore, in this study, the nano-silica was used to modify the asphalt binder. Nano-silica was added into the neat asphalt binder at concentrations of 2%, 4% and 6% by weight of the base asphalt binder. Rheological, chemical and morphological characterization of neat and modified asphalt binder was conducted to evaluate the performance of nano-silica modified asphalt binder. Following sections of the paper is devoted to description of materials and test methods including materials and sample preparation, aging procedure, dynamic rheological characterization and Fourier transform infrared spectroscopy (FTIR). The results of Physical properties of asphalt binder, dynamic rheological characterization and Fourier Transform Infrared Spectroscopy (FTIR) are presented in section 3. Dynamic rheological properties of asphalt binders are investigated based on three approaches including frequency sweep, temperature sweep and shear creep. Finally, the merit of application of nano-silica to improve anti-aging properties of asphalt binder is discussed.

Materials and Test Methods

This section will describe various materials used in this study as well as the sources of each material and its preparation method.

1) Materials and Sample Preparation

The base asphalt used in this study was AC 60/70 Pen grade.Asphalt binder was then blended with 2%, 4% and 6% nano-silica acquired through Neutrino Corporation located in Tehran, Iran. The quantity of each additive was selected by weight of based asphalt binder. The mixing was conducted using an IKA®bench top high shear mixer at 4000 rpm for 2 hours. To conduct the mixing, an aluminium can was filled with 250 – 260 g of asphalt and placed in a thermoelectric heater. When the asphalt temperature reached to 180o98 C, specified amount of nano-silica was added to the can and mixing for two hours. Using this procedure one neat sample and three nano-silica modified asphalt (NSMA) samples were produced. For simplicity in referring to each sample, they were named using following abbreviation: NEAT, NSMA-2%, NSMA-4% and NSMA-6%. To ensure nano-silica particles are dispersed uniformly within the asphalt matrix. The Scanning Electron Microscopy (SEM) images of asphalt were mainly used to understand the micro-structural changes of modified samples and to evaluate the matrix structure such as the physical dispersion of nano-silica particles (Kavussi and Barghabani, 2014). As can be clearly seen in FIGURE 1, nano-silica particles are well dispersed in the asphalt matrix.



(a) (b) (c)

FIGURE 1 SEM MICROSTRUCTURE IMAGES OF NANO-SILICA, NEAT AND NANO-SILICA MODIFIED ASPHALT AT18000X MAGNIFICATION, (A) NSMA-2%, (B) NSMA-4% AND (C) NSMA-6%

2) ***Aging Procedure***

All asphalt binder samples were aged by rolling thin film oven test (RTFOT) (ASTM D2872-85) in order to simulate the hot mixing process during plant production.

Dynamic Rheological Characterization

Dynamic Shear Rheometer (DSR) MCR101 from Austria Anton Paar Company was used in this study to measure complex modulus and complex viscosity. The repeated shear creep test with a loading and recovery period was conducted on each specimen. The creep tests were done under two fixed shear stresses of 100 and 3200 Pa for 10 cycles with 1s loading time and 9s of recovery time at 50˚C.

Fourier Transform Infrared Spectroscopy (FTIR)

Fourier Transform Infrared Spectroscopy (FTIR) spectra were recorded by Jasco IRT 3000 FTIR spectrometer. Infra-red spectra can be utilized in organic structure determination by identifying interatomic bonds in chemical compounds. Chemical bonds in different environments will absorb varying intensities and at varying frequencies. The frequencies at which there are absorptions of IR radiation referred to as peaks can be correlated directly to bonds within the material's chemical structure. Each interatomic bond may vibrate in several different motions (stretching or bending). Stretching absorptions usually produce stronger peaks than bending.

Results and discussion

Physical Properties of Asphalt Binder

1) ***Basic Physical Properties***

The effect of nano-silica modification on the conventional 128 asphalt binder rheological properties can be seen in TABLE 1. It can be observed that there is a decrease in penetration and an increase in the softening point when nano-silica was introduced to the asphalt binder. It was observed that all nano-modified asphalt samples had lower penetration and higher softening point than control asphalt. This in turn can lead to improvement in the asphalt binder stiffness and flexibility. However, the result of ductility test showed a declining trend in the presence of nano-silica. This can be attributed to the presence of high specific surface area in nano-silica which leads to increase of asphalt absorption.

TABLE 1 CONVENTIONAL PROPERTIES OF NEAT AND NANO-SILICA MODIFIED ASPHALT BINDERS

Sample	Penetration (mm)	Softening point (°C)	Ductility (cm)	Elastic recovery (%)
NEAT	58	47	>150	12
NSMA-2%	56	50.5	93	16
NSMA-4%	50	54.1	53	19
NSMA-6%	43	58	27	23

2) ***Storage Stability***

The storage stability results are listed in TABLE 2. The difference between the softening points was used to evaluate stability of the modified samples. The stability was deemed acceptable if the difference between the softening point of samples taken from the top and the bottom of the specimen was less than 2.5˚C.

TABLE 2 STORAGE STABILITY OF NEAT AND NANO-SILICA MODIFIED ASPHALT BINDERS

Sample	Softening Point (°C)		
	Top	Bottom	SP_{top} - SP_{Bottom}
NEAT	47.8	47.8	0
NSMA-2%	52.5	52.4	0.1
NSMA-4%	57.3	57.6	0. 3
NSMA-6%	61.9	91.6	0.6

TABLE 2 shows the softening points of the top and bottom specimens and the difference between these two temperatures. As can be observed from TABLE 2, the differences between the top and bottom softening points in all samples are less than 2.5˚C. This indicates that nano-silica modified specimens have appropriate storage stability. Therefore addition of nano-silica into asphalt will not negatively affect storage stability of the modified samples.

Dynamic Rheological Characterization

1) ***Frequency Sweep***

The relationship between frequency and temperature established by the Time-Temperature Superposition Principle (TTSP); this principle allows rheological properties of asphalt binders to be estimated over an extended frequency range. In FIGURE 2, complex modulus (G*) and phase angle (δ) values are presented in the form of black diagrams. Black diagrams provide a useful tool in analyzing rheological data for the identification of possible discrepancies in experimental results, and for the verification of time temperature equivalency in thermo-rheological simple materials (Airey, 2002). Black diagram curves corresponding to all asphalt binders have monotonic trend. As can

be clearly seen, the samples with higher concentration of nano-silica have lower complex modulus at higher phase angle and higher complex modulus at smaller phase angle. The RTFO aging slightly shifts all curves toward lower phase angle, thus indicating a change in rheological behaviour. In addition, comparison of Black diagram for RTFO aged and un-aged samples shows that specimens with high concentration of nano-silica are less susceptible to oxidative aging.

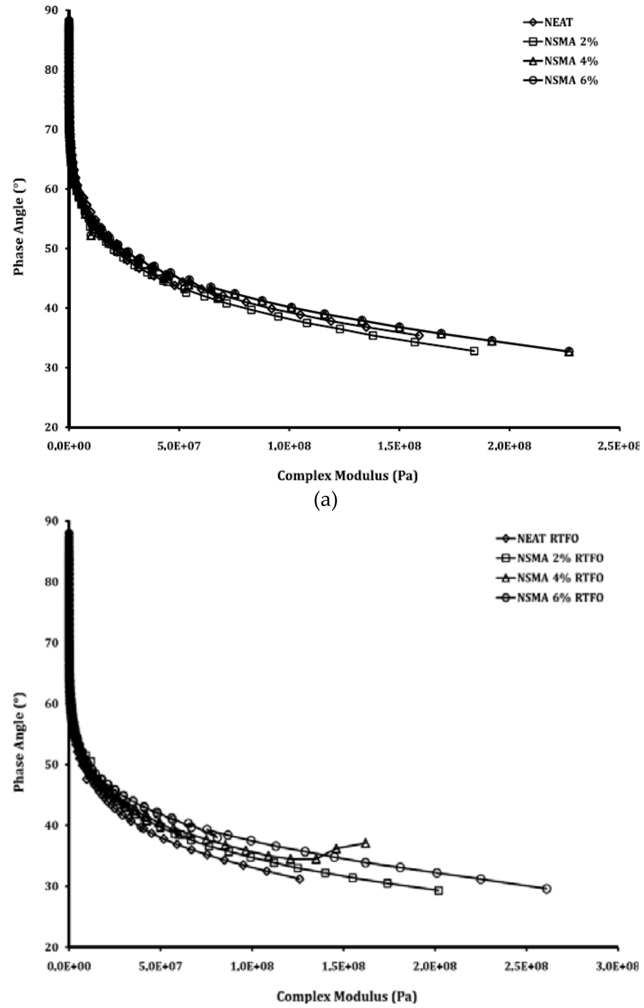


FIGURE 2 THE BLACK DIAGRAM OF ASPHALT BINDERS AT 30° C, (A) UN-AGED NEAT AND MODIFIED ASPHALT BINDER AND (B) AGED NEAT AND MODIFIED ASPHALT BINDER

2) *Temperature Sweep*

The values for the complex viscosity, complex modulus and phase angle of the nano-silica modified samples as a function of the nano-silica concentration and temperature at 10 rad/s (1.59 Hz) are shown in FIGURES 3- 5.

As it can be seen (FIGURE 3), asphalt complex viscosity increases with the increases in the nano-silica concentration. A nano-silica modified asphalt binder with high viscosity can lead to development of a thicker film surrounding the aggregates which increases the cohesive strength. This in turn can promote pavement durability.

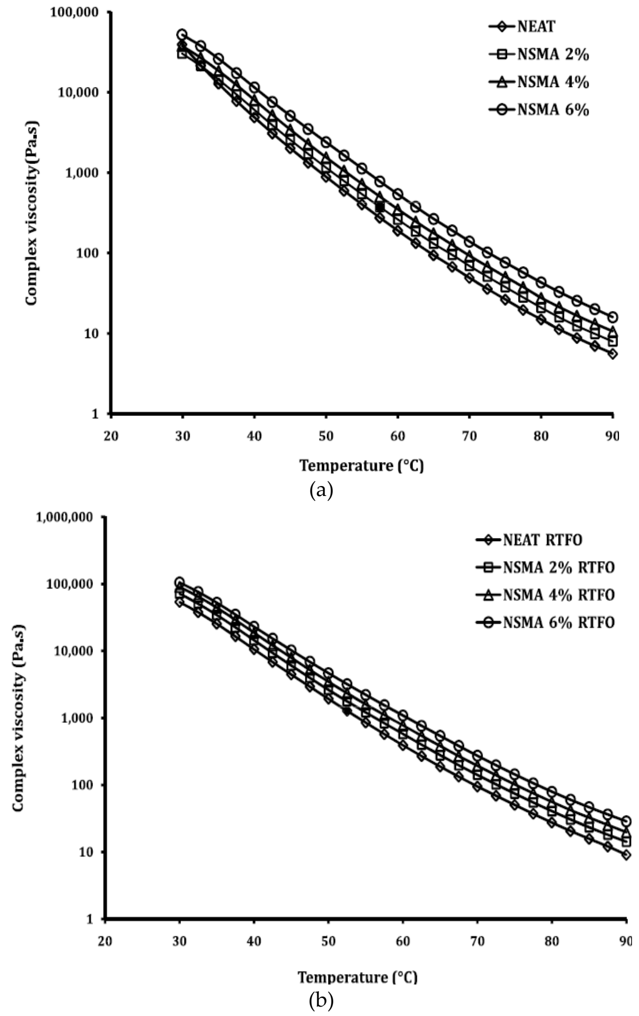
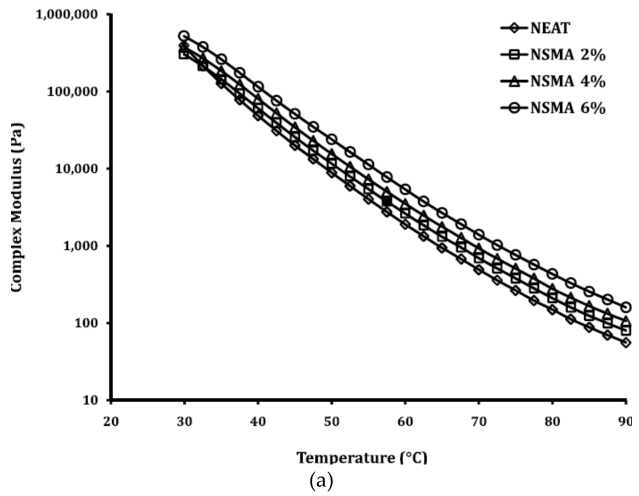
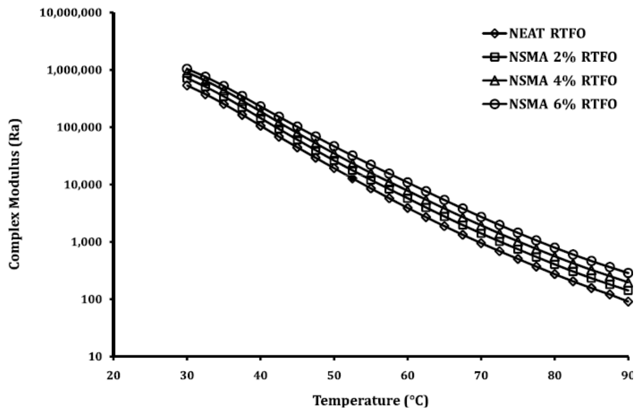


FIGURE 3 THE ISOCHRONAL PLOTS OF COMPLEX VISCOSITY VERSUS TEMPERATURE AT 10 RAD/S, (A) UN-AGED NEAT AND MODIFIED ASPHALT BINDER AND (B) AGED NEAT AND MODIFIED ASPHALT BINDER.

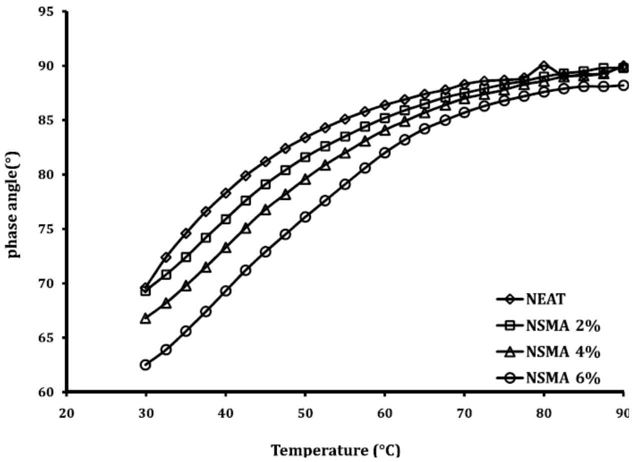




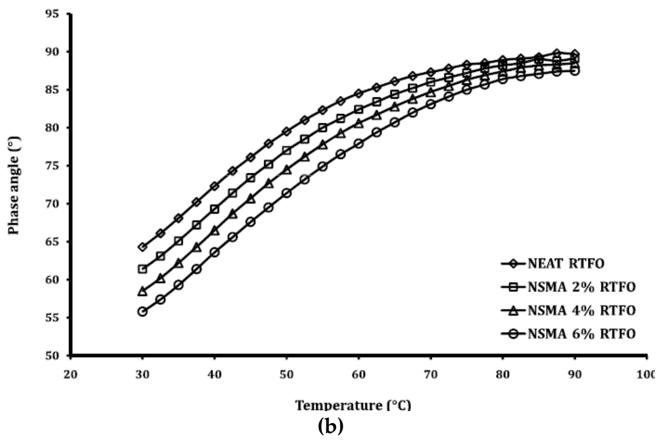
(b)

FIGURE 4 THE ISOCHRONAL PLOTS OF COMPLEX MODULUS VERSUS TEMPERATURE AT 10 RAD/S, (A) UN-AGED NEAT AND MODIFIED ASPHALT BINDER AND (B) AGED NEAT AND MODIFIED ASPHALT BINDER

FIGURE 4 indicates that the complex modulus of all modified samples were higher than those of the neat asphalt binder. In addition, it can be seen that phase angles of modified asphalt binder were all lower than those of base asphalt binder.



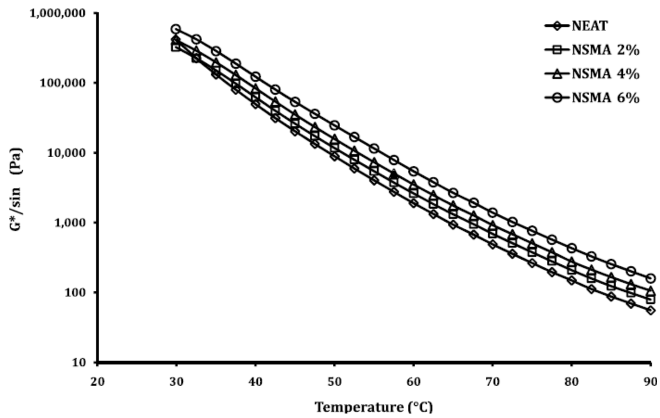
(a)



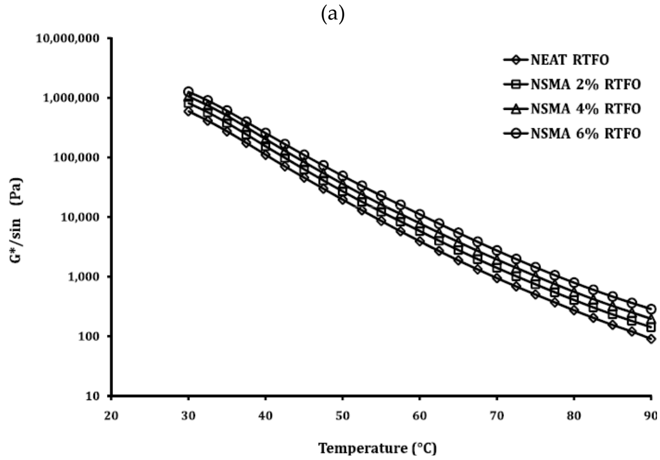
(b)

FIGURE 5 THE ISOCHRONAL PLOTS OF PHASE ANGLE VERSUS TEMPERATURE AT 10 RAD/S, (A) UN-AGED NEAT AND MODIFIED ASPHALT BINDER AND (B) AGED NEAT AND MODIFIED ASPHALT BINDER

Consequently, the modified asphalt binders were more elastic than neat asphalt binder and could enhance the asphalt rutting resistance. To further investigate asphalt performance in terms of permanent deformation (rutting); Superpave rutting parameter (G*/sinδ) was measured for both modified and non-modified specimens. Rutting is defined as the progressive accumulation of permanent deformation of each layer of the pavement structure under repetitive loading (Tayfur et al., 2007). FIGURE 6 shows the G*/sinδ versus temperature curves for (a) before and (b) after RTFO aging. The G*/sinδ values were calculated for the temperatures ranging from 30 to 90°C. The results show that introduction of nano-silica to the neat asphalt binder significantly increased the rutting parameter G*/sinδ; this in turn can enhance pavement resistance to permanent deformation. This can further allow extending the high temperature range within which asphalt binder could be used.



(a)



(b)

FIGURE 6 THE ISOCHRONAL PLOTS OF G*/SINΔ VERSUS TEMPERATURE AT 10 RAD/S, (A) UN-AGED NEAT AND MODIFIED ASPHALT BINDER AND (B) AGED NEAT AND MODIFIED ASPHALT BINDER

3) *Shear Creep*

The results of creep test at 50° C have been shown in FIGURE 7. At each loading cycle, the loading and recovery time was equal to 1 s and 9 s, respectively and loading cycles repeated for 20 times (10 cycles with 100 Pa loading and 10 cycles with 3200 Pa loading). Instantaneous elastic strain of asphalt developed during the loading stage, and the viscoelastic strain of asphalt was calculated as the total creep strain accumulated at the time of unloading. The instantaneouselastic strain of asphalt disappeared after unloading, and the delayed elastic strain recovered gradually (Wang, 2011). The unrecoverable viscoelastic strain is the permanent strain (Wang et al., 2011).Analysis of the data indicates that increasing the nano-silica content and aging in RTFO have noticeable effect on reducing the level of permanent strain. As shown in FIGURE 7 the trend is consistent among various cycles. However, the level of total permanent strain increases as the number of cycles increases.

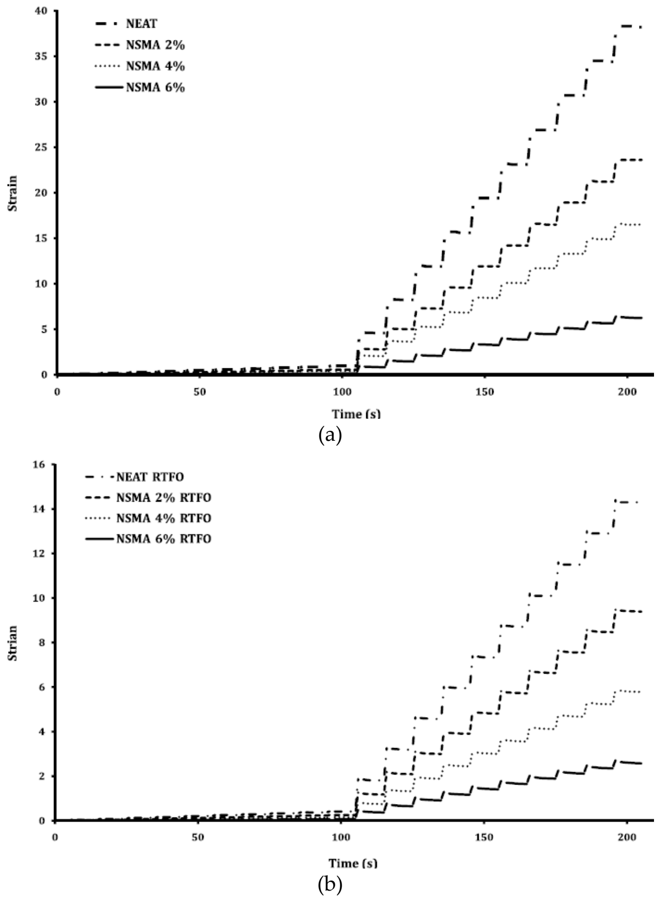


FIGURE 7 THE RESULTS OF CREEP TEST FOR UNMODIFIED AND MODIFIED SAMPLES AT 50° C, (A) UN-AGED NEAT AND MODIFIED ASPHALT BINDER AND (B) AGED NEAT AND MODIFIED ASPHALT BINDER

Fourier Transform Infrared Spectroscopy (FTIR)

The FTIR results show that nano-silica can improve the aging resistance of the bitumen as reflected in lower level of carboxylic acids (observed at 1400-1440 cm-1 related to O-H band) and sulfoxide (observed at ~1050 cm-1) in nano-silica modified specimen compared to those in non-modified specimens. Even though carboxylic acids naturally exist in asphalt, its concentration increases significantly due to oxidative aging (FIGURE 8). To further quantify the effect of nano-silica on reducing asphalt oxidative aging, carbonyl index was calculated for both nano-silica modified and non-modified specimens before and after RTFO aging. As shown in TABLE 3, the carbonyl index of aged nano-silica modified asphalt binder decreases as the percentage of nano-silica increases. Therefore, the nano-silica can be a promising candidate for delaying oxidative aging of asphalt binder.

TABLE 3. CARBONYL INDEX OF AGED AND UNAGED MODIFIED BITUMEN

Unaged	C=O(1690cm^{-1})	**Aged**	C=O(1690cm^{-1})
neat bitumen	0.082	neat bitumen	0.095
bitumen+2% nanosilica	0.044	bitumen+2% nanosilica	0.055
bitumen+2% nanosilica	0.039	bitumen+2% nanosilica	0.041
bitumen+2% nanosilica	0.052	bitumen+2% nanosilica	0.031

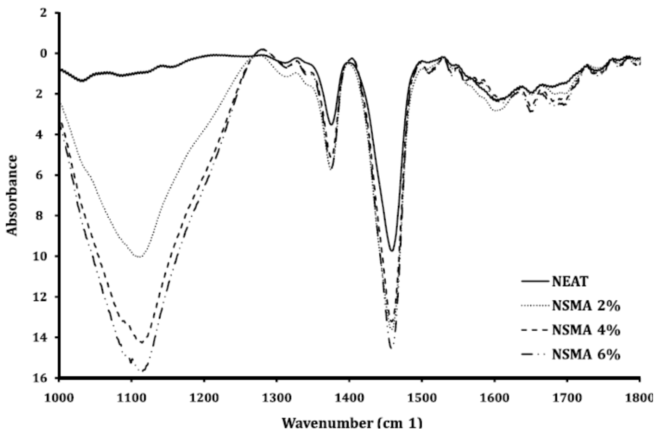


FIGURE 8 FTIR SPECTRA ANALYSIS OF NEAT AND MODIFIED ASPHALT BINDER (A) UN-AGED ASPHALT BINDERS AND (B) AGED ASPHALT BINDERS

Conclusion

This paper investigates the merit of application of nano-silica in asphalt binder as an anti-aging additive. To investigate the effectiveness of the nano-silica in reducing asphalt aging, different percentages of nano-

silica were added to neat asphalt binder. Asphalt binder was then exposed to short term oxidative aging using a rolling thin film oven (RTFO). To study the change in the chemical, rheological and morphological properties of asphalt binders in presence of nano-silica, the Superpave™ tests and Fourier transform infrared spectroscopy (FTIR) were conducted. Rheological characterization of modified and non-modified asphalt binder showed introduction of nano-silica enhances the rheological properties of neat binder by increasing its storage modulus and elasticity. This in turn can lead to improvement of pavement rutting resistance. Furthermore, the FTIR spectrums showed that introduction of nano-silica can delay the oxidative aging process; this was reflected in the reduction of the rate of carboxyl formation after aging as measured by carbonyl index. Therefore, the study concluded that nano-silica can be a promising candidate to be used as an anti-aging additive in asphalt while enhancing asphalt rutting resistance.

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